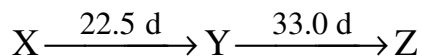


From Atkins: 11.7, 11.9, 11.12 and 11.24 (extra)

11.7) Two radioactive nuclides decay by successive 1st-order processes:



At what stage after X is first formed will Y be most abundant?

Working with Eq.(11.4b) and Fig. 11.3, one obtains Eq.(11.5) by taking the 1st derivative of Eq.(11.4b) with respect to the concentration of the intermediate and setting this result equal to zero. This then locates the maximum in the [I] vs. time function in Fig. 11.3.

$$t = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad (11.5)$$

From the half-lives of each step and knowing that they are both 1st-order reactions,

$$t_{1/2} = \frac{\ln 2}{k}, \quad \text{and} \quad k_1 = \frac{\ln 2}{22.5 \text{ d}} = 0.030807 \text{ d}^{-1}$$

$$k_2 = \frac{\ln 2}{33.0 \text{ d}} = 0.021004 \text{ d}^{-1}$$

$$\text{so, } t = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} = \frac{1}{0.030807 - 0.021004} \ln \frac{0.030807}{0.021004}$$

$$= 39.1 \text{ days}$$

11.9) The reaction mechanism



involves an intermediate A. Deduce the rate law for the formation of P.

$$\text{For the 2nd step: } \frac{d[P]}{dt} = k_2[A][B]$$

The rate law for the 2nd step in terms of the production of P is what we will work with to obtain the overall rate law (since this is also in terms of production of P)

To get rid of the intermediate A in this rate law, we could use the steady state approximation, but you'd find that you'd get a nasty looking quadratic in [A].

Alternatively, since the slow step (2nd) is preceded by a fast step (1st), we can safely assume that the 1st step will reach equilibrium (a "pre-equilibrium")

From step 1: $K = \frac{[A]^2}{[A_2]}$, and thus $[A] = K^{\frac{1}{2}}[A_2]^{\frac{1}{2}}$

Substituting into the rate law above, $\frac{d[P]}{dt} = k_2 K^{\frac{1}{2}} [A_2]^{\frac{1}{2}} [B]$

11.12) The condensation reaction of acetone, $(CH_3)_2CO$, in aqueous solution is catalyzed by bases, B, which react reversibly with acetone to form the carbanion $C_3H_5O^-$. The carbanion then reacts with a molecule of acetone to give the product. A simplified version of the mechanism is:



where AH or HA stands for acetone and A^- is its carbanion. Use the steady state approximation to find the concentration of the carbanion and derive the rate equation for the formation of the product.

Write the rate law for each step : (note: you have a choice, but I'll write them in terms of the carbanion, since we're going to use the ss approximation to get rid of it)

$$(1) \frac{d[A^-]}{dt} = k_1[AH][B]$$

$$(2) -\frac{d[A^-]}{dt} = k_2[A^-][BH^+]$$

$$(3) -\frac{d[A^-]}{dt} = k_3[A^-][HA] = \frac{d[\text{product}]}{dt}$$

Employ the steady state approximation for A^- :

$$\frac{d[A^-]}{dt} \approx 0 = k_1[AH][B] - k_2[A^-][BH^+] - k_3[A^-][HA]$$

$$\text{Solving for } [A^-] : [A^-]_{ss} = \frac{k_1[AH][B]}{k_2[BH^+] + k_3[HA]}$$

Substituting into the rate equation for formation of product in step (3):

$$\frac{d[\text{product}]}{dt} = \frac{k_1 k_3 [AH]^2 [B]}{k_2 [BH^+] + k_3 [HA]}$$

11.29) In a photochemical reaction $A \rightarrow 2B + C$, the overall quantum yield with

500 nm light is $2.1 \times 10^2 \text{ mol einstein}^{-1}$. After exposure of 300 mmol A to the light, 2.15 mmol B is formed. How many photons were absorbed by A ?

The definition of the overall quantum yield is: $\Phi = \frac{\# \text{ moles that react}}{\text{einsteins of radiation absorbed}}$

Based on the stoichiometry of the reaction, the formation of 2.15 mmol of B means

that $\frac{2.15}{2}$ mmol of A reacted.

$$\text{Hence, } \Phi = 2.1 \times 10^2 = \frac{2.15 \times 10^{-3} / 2}{\text{einsteins absorbed}}$$

$$\text{einsteins absorbed} = \frac{2.15 \times 10^{-3} / 2}{2.1 \times 10^2} = 5.119 \times 10^{-6} \text{ einsteins}$$

$$\begin{aligned} \# \text{ photons absorbed} &= 5.119 \times 10^{-6} \text{ einsteins} \times \frac{6.02214 \times 10^{23} \text{ photons}}{\text{einstein}} \\ &= 3.1 \times 10^{18} \text{ photons absorbed} \end{aligned}$$